AFOSR FINAL REPORT

Principal Investigator:
 Tsu-Wei Chou
 Department of Mechanical Engineering
 Department of Materials Science and Engineering
 Center for Composite Materials
 University of Delaware, Newark, DE 19716
 Tel: (302) 831-2421
 Fax: (302) 831-3619

Co-Principal Investigator:
 Erik T. Thostenson
 Department of Mechanical Engineering
 Department of Materials Science and Engineering
 Center for Composite Materials
 University of Delaware, Newark, DE 19716

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Multifunctional Carbon Nanotube–Based Sensors for Damage Detection and Self Healing in Structural Composites

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14. ABSTRACT
During the past year of the research program focusing on developing composites with damage sensing and self-healing functionalities based on carbon nanotubes, improvements to the state-of-the-art in nanocomposite processing have been made. In order to accommodate the processing of thick-section composites, an alternative approach to the traditional calandering method of carbon nanotube dispersion has been developed. A fiber sizing agent containing multiwalled carbon nanotubes was used in the processing of conductive E-glass fabric composites, which were demonstrated to undergo measurable, non-reversible changes in resistivity during the accumulation of damage under quasi-static loading scenarios. These conductively-modified composites possess the potential to sense damage under fatigue tensile and dynamic compressive and impact loadings. A review article describing the design, processing and resultant mechanical, electrical and thermal properties of nanotube-based composites has been published.

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I. Introduction

In Year-1 of the research program, focusing on the development of carbon nanotube multifunctional *in situ* sensing approaches for detecting damage in composites, we have initiated research in processing of nanostructured composites and examined their resistance/deformation relations and fabricated large-scale nanotube/fiber composites for detecting damage accumulation. In addition, we have initiated modeling research to elucidate the influence of nanoscale structure on the percolation and electrical conductivity of nanotube-based composites. Major accomplishments include the writing of a custom data acquisition program integrating real-time load, strain gage measurements and resistance measurements. This system has been used to detect damage accumulation in composite laminates in situ under quasi-static uniaxial and cyclic loading conditions. Large resistance changes that occur when re-loading a damaged specimen may be a measure of the extent of damage. For the purpose of studying continuum percolation of nanocomposites with wavy nanotubes, we proposed a simple yet versatile method for identifying percolation of arbitrary shape fillers within composites. The current effort focuses on the two dimensional percolation phenomena of nanocomposites.

In Year-2 of the research program, we have established a parameter for quantifying microstructural damage based on the loading/unloading resistance response of a damaged composite specimen. In addition, we have established a modeling technique capable of elucidating the influence of nanoscale structure on the percolation and electrical conductivity of nanotube-based composites toward establishment of the basis for optimization of *in situ* sensing. Major accomplishments include establishment of a methodology for quantifying the microstructural damage under static and dynamic loading conditions through real-time sensing. Large resistance changes that occur when re-loading a damaged specimen can be a quantitative measure of damage and the transition between microcracking and delamination modes can be detected. For modeling of nanocomposite electrical properties, an efficient technique has been developed to examine the influence of nanotube waviness and contact resistance on the electrical resistivity. In addition, a highly efficient method was developed for backbone identification by directly employing the definition of a backbone as the current-carrying part of a resistor network.

In Year-3 of the research program, we have established that the damaged resistance parameter can be utilized as a quantitative measure of damage. Careful measurements of damaged resistance and microscopic edge replication under cyclic loading reveal damaged resistance is a linear function of crack density. Co-acoustic emission and nanotube sensing have also been shown to track the progression of microcracking and delamination in real-time. Modeling work has further established the ability to understand the physics of electrical percolation and its application for in situ damage sensing. Major accomplishments include the establishment of the quantitative nature of the damaged resistance parameter as a direct function of crack density. The co-acoustic emission and nanotube damage sensing have been established to provide information of cracking and delamination in real-time and also provide validation that resistance changes are due to the formation of micro-cracks. For modeling of nanocomposite electrical properties a highly efficient method for backbone structure and conductivity has been established. The influence of nanotube orientation and the damage sensing process have been modeled for cross-ply composites.

During the last year of the research program, focusing on developing composites with damage sensing and self-healing functionalities based on carbon nanotubes, improvements to the state-of-the-art in nanocomposite processing have been made. In order to accommodate the processing of thick-section composites, an alternative approach to the traditional calendering method of carbon nanotube dispersion has been developed. A fiber sizing agent containing multiwalled carbon nanotubes was used in the processing of conductive E-glass fabric composites, which were demonstrated to undergo measurable, non-reversible changes in resistivity during the accumulation of damage under quasi-static loading scenarios. These conductively-modified composites possess the potential to sense damage under tensile fatigue and dynamic compressive and impact loadings. A review article describing the design, processing and resultant mechanical, electrical and thermal properties of nanotube-based composites has been published.

Recent efforts include the development of self-healing composites using integrated vascular resin delivery systems. Toward this end, nanotube-based composites with microchannels were processed and evaluated under quasi-static tensile loading. We demonstrated that carbon nanotube/resin injection after loading and damage formation resulted in the re-establishment of electrical contact through resistivity measurements (Fig. 1) and that this resulted in modulus recovery of the composite (Fig. 2).
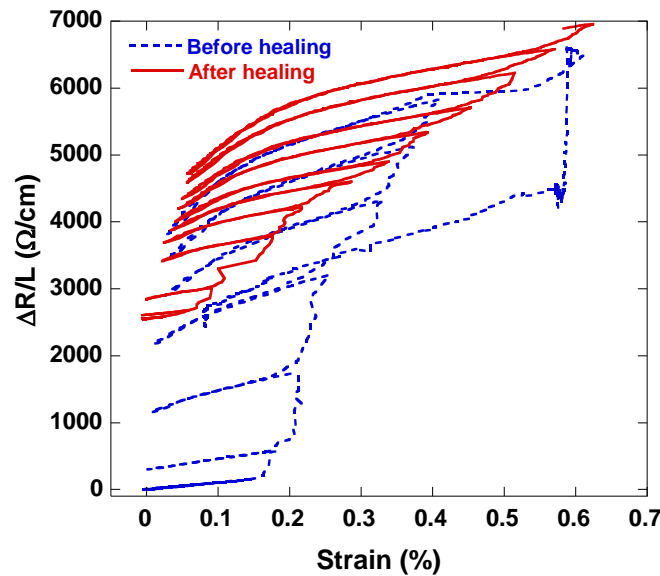

Fig. 1. Resistance recovery after healing in a composite specimen evaluated under quasi-stationary cyclic tensile loading
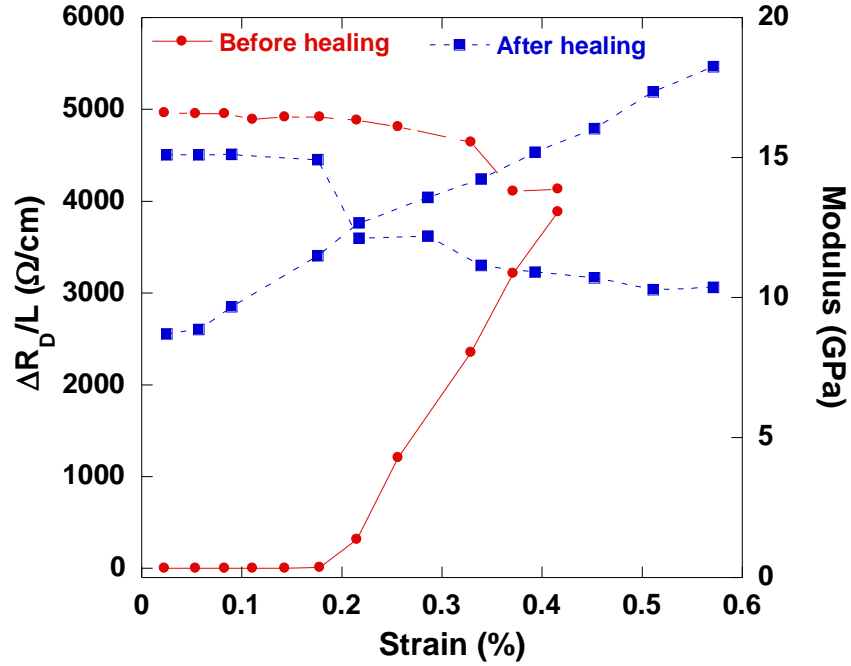
Fig. 2. Modulus recovery in a composite after nanotube-infused resin injection

II. Brief Overview of Accomplishments

During the prior four-year grant period, numerous research topics pertaining to the development and implementation of self-sensing carbon nanotube-based composites have been explored. Several manuscripts were published; their content is summarized here.

A. Electrical Percolation in Epoxy Resin using Carbon Nanotubes

Due to their high aspect ratio (length/diameter), carbon nanotubes are able to form electrically percolating networks within nonconductive resins. We demonstrated this in 2006 [1] by dispersing multi-walled carbon nanotubes in epoxy resin at weight fractions ranging between 0 and 1.0%. Electrical percolation occurs at 0.1 wt% carbon nanotube addition and volume resistivity as low as 10^3 $\Omega \cdot$cm are achieved in nanocomposites containing 1.0 wt% nanotubes (Fig. 3).
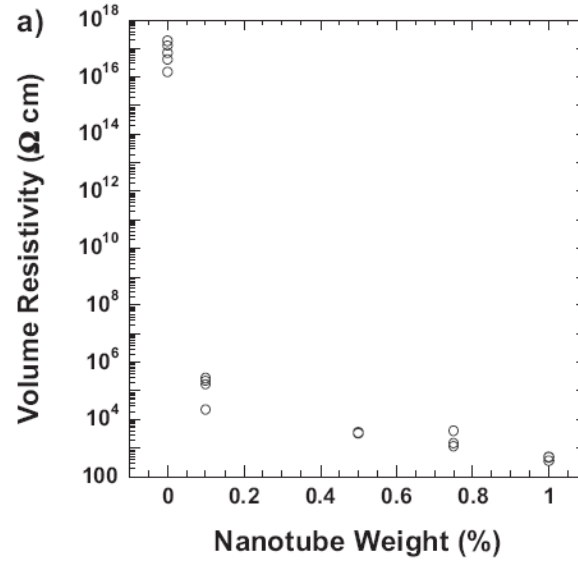
Fig. 3. Electrical percolation behavior in nanotube-epoxy composites [1]

B. Carbon Nanotube Composite Processing

In order to achieve electrical percolation in composites containing low concentrations of carbon nanotubes, it is necessary to preserve the aspect ratio of the nanotubes during processing [1]. A uniform distribution of carbon nanotubes in an epoxy resin has been accomplished using a high shear stress field [2]. This method of dispersion incorporates a calendering approach through which large agglomerates of nanotubes can be broken down while the aspect ratio is maintained [Adv. Mater 2006]. The three-roll mill used for dispersion is shown in Fig. 4.
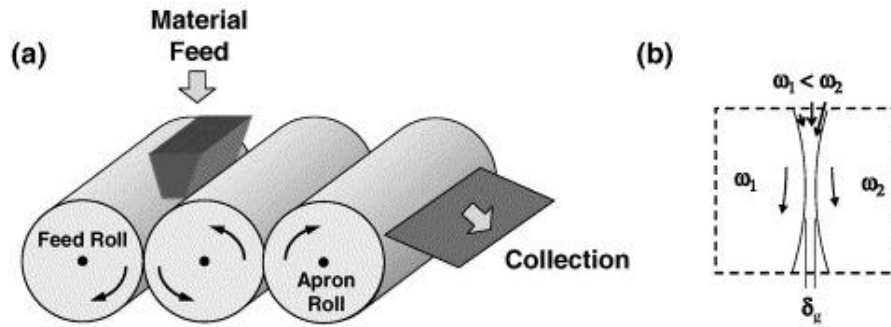

Fig. 4. (a) Three-roll mill used in carbon nanotube dispersion and (b) region of high shear mixing between the feed and center rolls [2]

We recently explored a second approach to modifying the conductivity of fiber composites with carbon nanotubes. In this method, a fiber sizing agent containing multi-walled carbon nanotubes was used to develop composites with agglomerated regions of nanotubes at the fiber surface [3]. An image of the nanotube coating on the surface of two E-glass fibers is shown in Fig. 5.
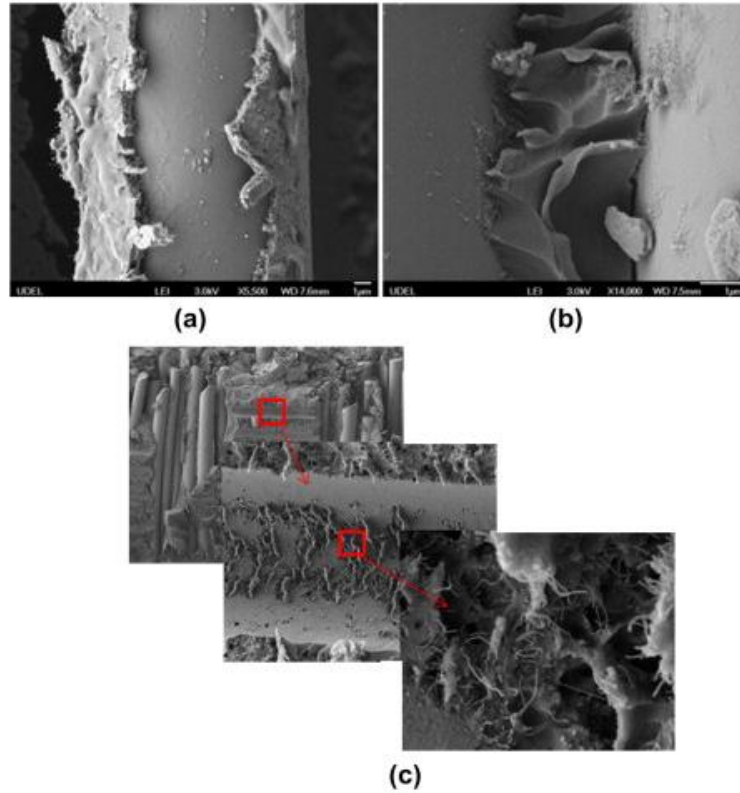
Fig. 5. (a) Carbon nanotube agglomerates on the surface of glass fibers in the composite; (b) Nanotube agglomeration in the inter-fiber region; (c) Nanotube agglomeration in the matrix [3]

Figure 6 presents a schematic comparison of the different microstructural configurations resulting from the calendering approach vs. the sizing approach. The electrical conductivity of carbon nanotube composites processed via calendering and sizing methods is compared to the conductivity of carbon fiber-based composites in Fig. 7, demonstrating that the nanotube sizing agent significantly improves the electrical conductivity of glass fiber composites. This method of conductive modification has applicability for large structures, in which viscosity-related issues could otherwise arise during infusion.
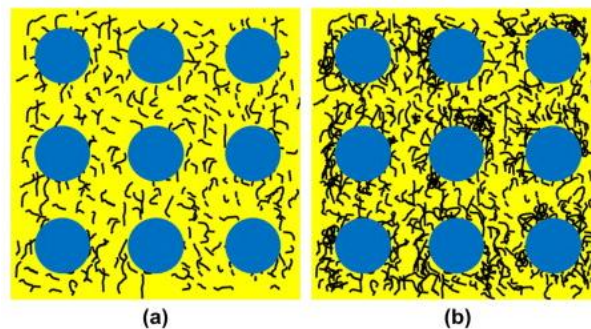

Fig. 6. Schematics showing (a) Nanotubes evenly distributed in the matrix using the three-roll mill process; (b) Nanotube agglomeration of the surface of sized fibers [3]
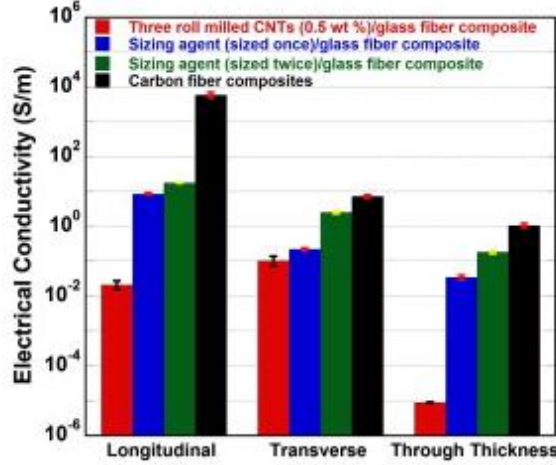
Fig. 7. Comparative study of electrical conductivity of three-roll milled carbon nanotube (0.5 wt%)/glass fiber/epoxy composite, glass fiber/sizing agent (sized once)/epoxy composite, glass fiber/sizing agent (sized twice)/epoxy composite and carbon fiber/epoxy composite.

C. Numerical Simulations of Electrical Percolation

1. Waviness Effect

Understanding the effect of filler shape on the electrical percolation threshold is critical in the design of electrically conductive nanocomposites [4-8]. Carbon nanotubes have high aspect ratios which lead to varied geometries, adding a layer of complexity to this issue. To begin with, the continuum percolation of nanocomposites with fillers of arbitrary shapes (Fig. 8) was studied using two-dimensional Monte Carlo (MC) simulations.
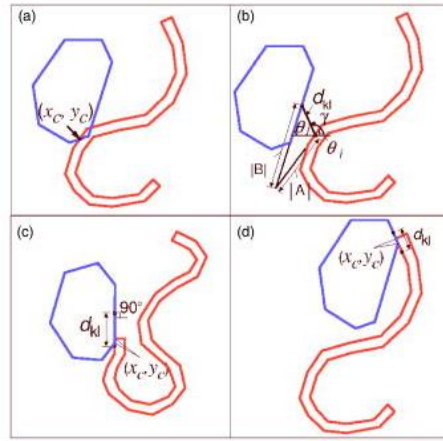

Fig. 8. Contact patterns for fillers with arbitrary shapes [9]

The percolation threshold is simulated for nanotubes of varying waviness, represented by the curl ratio, $\lambda = L_{real}/L_{effective}$. We demonstrate that an increase in aspect ratio of the nanotube reduces the percolation threshold. Additionally, the percolation threshold of wavy nanotubes increases with increasing curl ratio, but the effect of curl ratio tends to decrease slightly with the increase of nanotube aspect ratio [9].
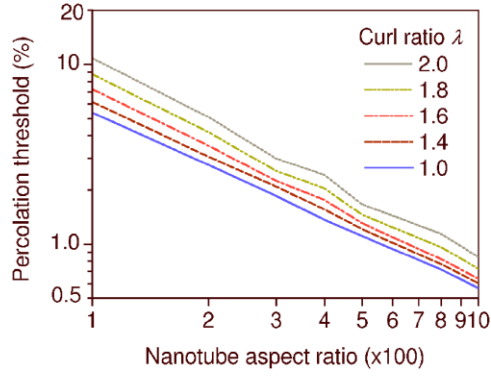
Fig. 9. Effect of nanotube waviness on percolation threshold [9]

This model was expanded to consider the effect of tunneling resistance due to an insulating film of matrix material between crossing nanotubes (Fig. 10). The resulting effect of nanotube waviness on electrical conductivity is plotted in Fig. 11. The contact resistance in these simulations is assumed to be the same for all contact points. The specimen size is taken as 20 μm × 20 μm and the nanotube aspect ratio is 1000 (diameter 2 nm, length 2 μm) [10]. It can be seen that the electrical conductivity of composites increases with increasing nanotube concentration for both straight and wavy nanotubes. The electrical conductivity of composites with wavy nanotubes is lower than that of composites with straight nanotubes.
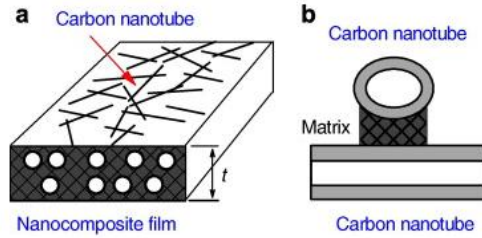

Fig. 10. Computational model of contact resistance of crossing nanotubes. (a) A nanocomposites film; (b) an insulating matrix in the contact area [10]
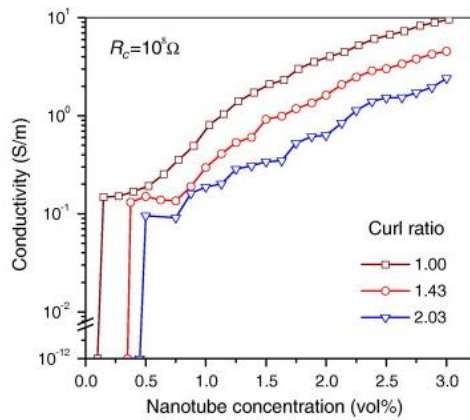

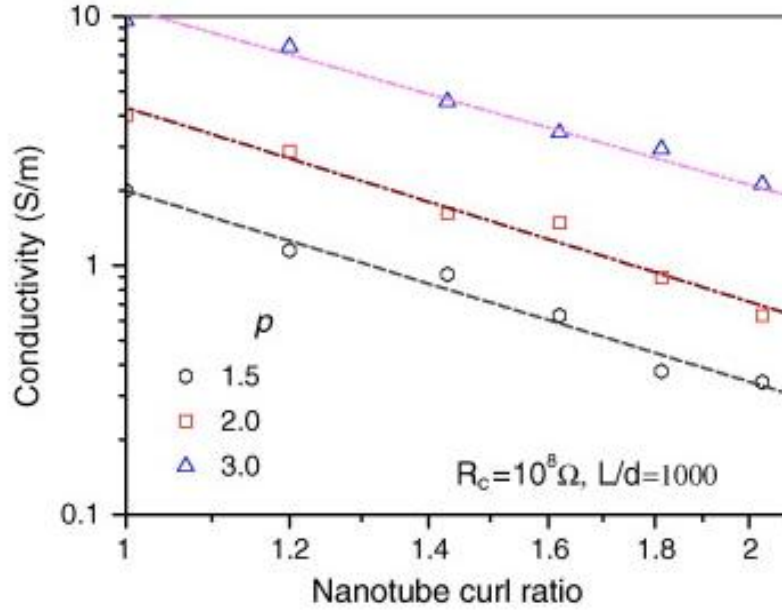Fig. 11. Effect of nanotube waviness on electrical conductivity [10]

Fig. 12. Power-law relationship between conductivity and nanotube curl ratio [10]

The effect of nanotube concentration (ρ) is accounted for in Fig. 12. The electrical conductivity gradually decreases with increasing nanotube curl ratio for a given nanotube concentration [10].

In summary, a carbon nanotube-based composite film is taken as a representative cell of a multilayered nanocomposite and is modeled in order to study the effect of nanotube waviness on the nanocomposite electrical conductivity. Results of Monte Carlo simulations indicate that the nanotube waviness has a significant effect on the electrical conductivity. Although the electrical conductivity of composites increases with increasing nanotube concentration for both straight and wavy nanotubes, the electrical conductivity of composites with wavy nanotubes is much lower than that of composites with straight nanotubes. The critical exponent of the power-law dependence of electrical conductivity on the nanotube concentration decreases with increasing nanotube curl ratio. There is a logarithmically linear relationship between the conductivity and the nanotube curl ratio, i.e., the conductivity exhibits an inverse power-law dependence on the curl ratio with a critical exponent in the range of 2.2–2.6 [10].

2. Electrical Tunneling Distance

In order to determine the maximum tunneling gap in carbon nanotube-based composites and the effect of tunneling gap on contact resistance, a computational model of a representative layer of a nanocomposite was developed [11]. In this model, the composite layer is simulated as a pseudo-three-dimensional problem in which the CNTs of diameter d are distributed in two stacking tube layers (Fig. 13).
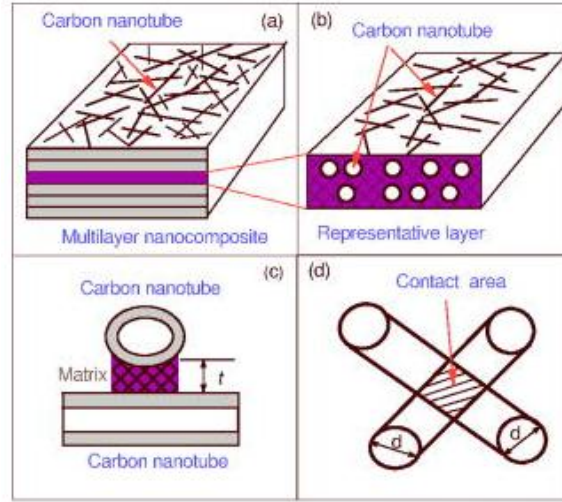
Fig. 13. Computational model of contact resistance of crossing nanotubes in a composite with an insulating film in between. (a) An illustration of multilayer nanotube-based composites. (b) A representative layer. (c) Intertube insulating matrix of thickness *t* in the contact area. (d) Two crossing nanotubes of diameter *d* [11]

The calculated tunneling resistance is plotted as a function of the thickness of the insulating layer and carbon nanotube diameter (Fig. 14). In our calculations, the work function of carbon nanotubes is taken as 5.0 eV [12] and the dielectric constants are K = 3.98 for epoxy and K = 4.5 for alumina. The thickness of the insulating layer between crossing carbon nanotubes strongly affects tunneling resistance. The nanotube diameter has a moderate effect on the tunneling resistance: the larger the tube diameter is, the lower the tunneling resistance is. The use of matrix material (either polymeric or ceramic) appears unimportant due to the small difference in their dielectric constants. However, the tunneling resistivity actually increases with an increasing dielectric constant in the insulating film [13].
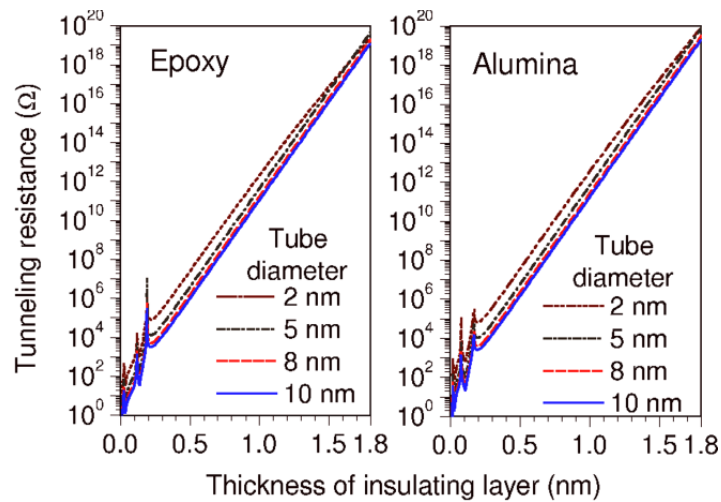

Fig. 14. Contact resistance due to the electric tunneling effect in carbon nanotube/epoxy or alumina composites [11]

In summary, by employing Simmons' formula for calculating the contact resistance of crossing carbon nanotubes separated by an insulating layer and simulating the electrical conductivities of percolating nanotube networks, we conclude that the maximum tunneling distance in nanotube-based polymeric or ceramic composites is about 1.8 nm. Simulation results indicate that the contact resistance plays a dominant role in CNT composite films, in contrast to the dominant role of the intrinsic resistance of carbon nanotubes in nanotube mats. The electrical conductivity of percolating carbon nanotube networks in composite films follows the scaling law and the critical exponent depends on the level of contact resistance [11].

3. Carbon Nanotube Backbone Identification

In order to improve the current percolation theory, a new algorithm for identifying backbones was developed [14]. This algorithm is based on the current-carrying definition of backbone and is carried out on a predetermined spanning cluster (Fig. 15). The conductivity of the percolating system can be obtained through the same process as the backbone identification. Monte Carlo simulations confirm the effectiveness of the algorithm.
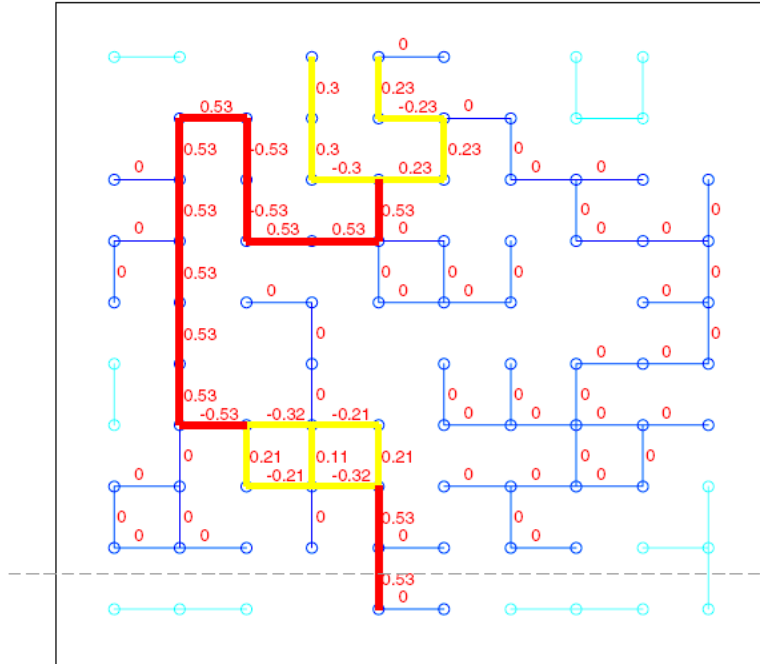

Fig. 15. An example of identified backbone (text: electric current value, positive directions are ↓ and ←; color: red-red bonds, yellow-blobs, blue-dangling bonds; dash line: section for determining the total current) [14]

D. Carbon Nanotube Failure Behavior

Electromechanical coupling in single-walled carbon nanotubes has been studied theoretically. The charge distribution on single-walled carbon nanotubes in an electric field is obtained by an atomistic moment method based on classical electrostatics theory. The electrostatic interactions between charged carbon atoms are calculated using the Coulomb law. The charge-induced deformations of single-walled carbon nanotubes in axial and radial directions are obtained by

using the molecular structural mechanics method and considering the electrostatic interactions as external loads acting on carbon atoms. The electrical failure of charged carbon nanotubes is found to be controlled by the charge level and also affected by the caps on the nanotube ends. The results indicate that the bond breaking first appears at the tube ends and the end-caps can enhance the stability of the nanotubes [15].

For determining the charge distribution on the nanotube, we employ an atomistic moment method, recently developed by the authors [16]. In this method, the classic electrostatic theory is applied to the nanoscale structures. The surface of a nanotube is partitioned into numerous subareas, with a carbon atom at the center of each subarea (Fig. 16). The charge distributed in a subarea is assumed to be uniform and can be summed up as a point charge concentrating on the associated atom. The point charges on all the atoms can be obtained by solving a system of algebraic equations, which are established based on the concept of equipotential surface. The effect of nanotube length on the critical charge level is plotted in Fig. 17.
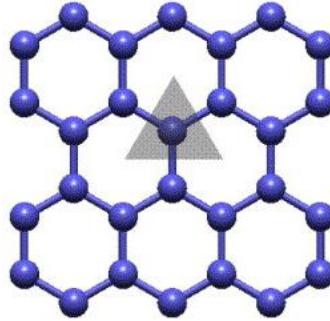

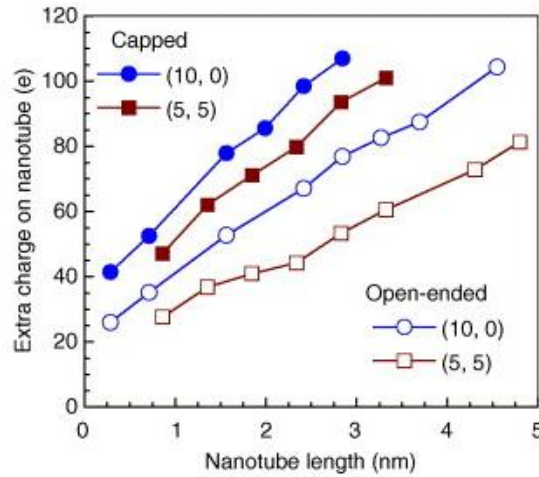Fig. 16. Electric charge distributed on a triangular area surrounding a carbon atom [15]

Fig. 17. The effect of nanotube length on the critical charge level [15]

E. Carbon Nanotube Networks for Damage Sensing in Composites

Initially, nanocomposites consisting of epoxy resin and 0.5 wt% multi-walled carbon nanotubes were evaluated under quasi-static tensile loading. These specimens were shown to exhibit increases in resistance consistent with increases in strain during loading [1]. The mechanical and electrical behavior of a nanocomposite is shown in Fig. 18.
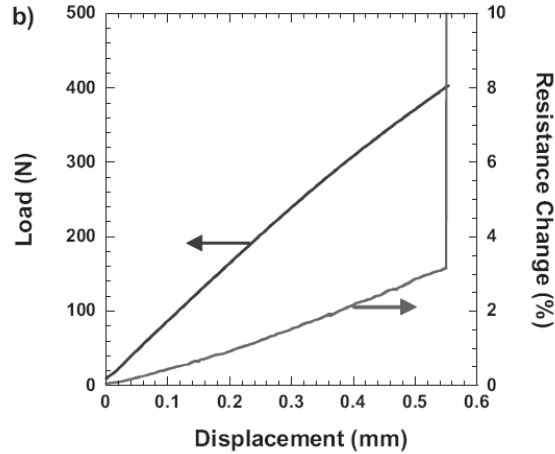

Fig. 18. Resistance change with deformation for a 0.5 wt% nanotube-epoxy composite loaded in tension [1]

Building on this success, we processed five-ply unidirectional E-glass composites in which the center ply of the laminate was cut in the middle of the specimen to promote ply delamination during tensile testing [1]. Fig. 19 shows the mechanical and electrical response of this specimen type. The specimen resistance increases linearly with initial deformation and is consistent with the previous observation of resistance-strain response (Fig. 18). Once ply delamination is initiated, the resistance increases drastically, marked by a progressive increase in resistance slope with extension.

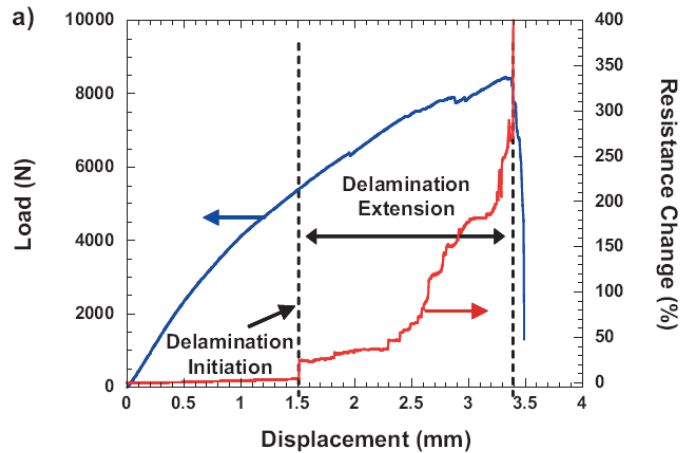Fig. 19. Load-displacement and resistance curves for 0° specimen with center ply cut to initiate delamination [1]

The effect of transverse microcracking on the resistance behavior was investigated using [0/90]$_s$ cross-ply specimens with plies oriented along the loading axis (0°) on the outside of the laminate and the 90° plies at the center. These specimens initially experienced a linear increase in

resistance, again similar to the nanocomposite (Fig. 20). However, resistance increases abruptly in a step-like manner - this is attributed to microcrack formation in the 90° layers.
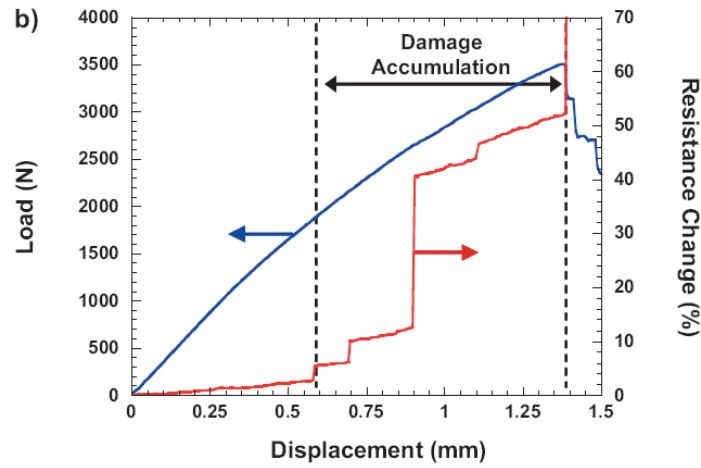

Fig. 20. Load-displacement and resistance curves for the 0/90 specimen [1]

The response of this composite was further analyzed by comparing the resistance behavior during first loading with that of a second loading cycle (Fig. 21). Resistance is shown to increase by 20% during the first loading and to return to nearly the initial value upon unloading. Upon reloading, the specimen experiences sharp increases in resistance at much lower levels, corresponding to the reopening of microcracks. This is a clear indicator of permanent damage to the composite. By providing a quantitative means of damage detection in composites, this approach presents the opportunity to evaluate the effectiveness of self-healing methodologies.
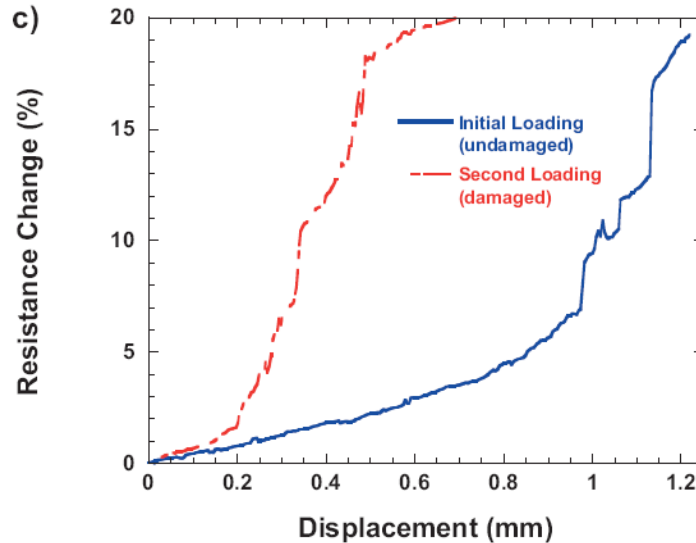

Fig. 21. Resistance curves for initial loading (undamaged) and reloading (damaged) laminates [1]

The evolution and accumulation of damage in fiber composites can be detected using a percolating carbon nanotube network [17]. E-glass/epoxy composites [0/90]$_s$ were infused with

carbon nanotubes and evaluated under quasi-static cyclic tensile loading. the electrical and mechanical response is shown in Fig. 22.
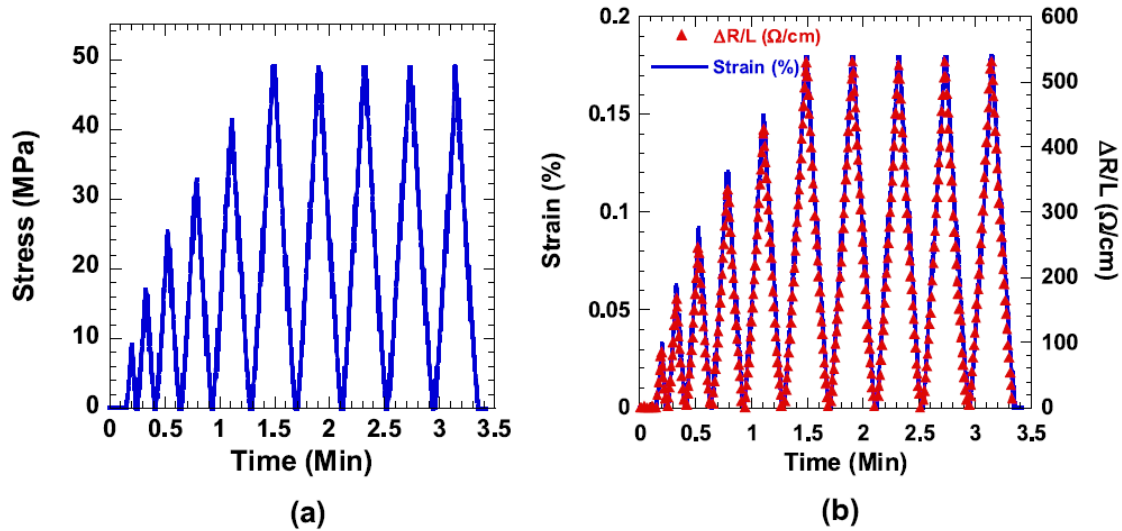
Fig. 22. (a) Cyclic loading stress profile applied to the specimen showing increasing loading to constant stress level and (b) the instantaneous response of resistance with strain [17]

In Fig. 22, the strain level is below that at which microstructural damage occurs; this is confirmed by the consistent baseline resistance - meaning that, after unloading, resistance returns to its initial value. Increasing the level of strain results in damage within the composite; this is show in the scanning electron micrographs in Fig. 23 and is confirmed by an increase in the resistance baseline value. Here, resistance measurements provide not only a measure of irreversible damage; the nonlinear resistance behavior also indicates elastic deformation and crack re-opening (Fig. 24).
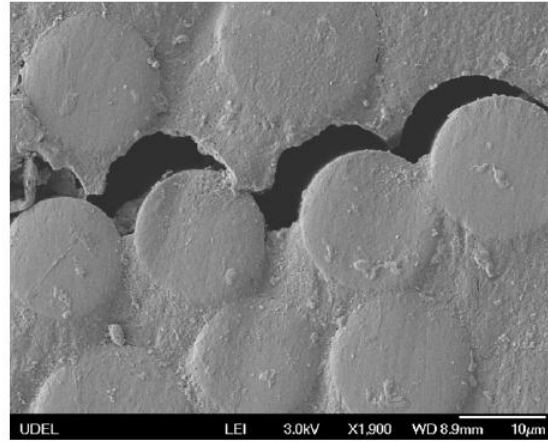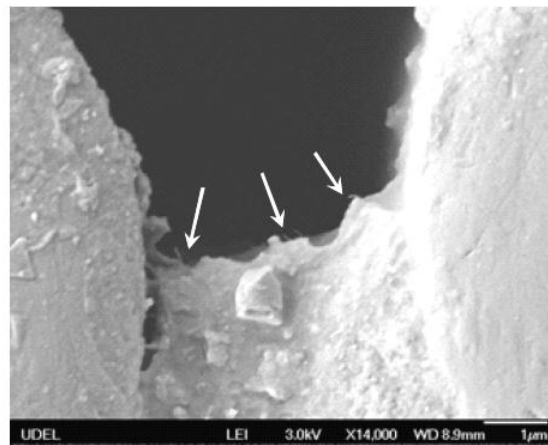
Fig. 23. SEM images showing (a) formation of a microscale crack in a 90º ply and (b) carbon nanotubes protruding from the matrix in the region between two fibers [17]

Fig. 24. (a) Cyclic loading of a cross-ply laminate to ultimate fracture showing the transient resistance and strain response and (b) Expanded view of the fifth loading cycle highlighting the nonlinearity of the resistance response and re-opening and formation of cracks [17]

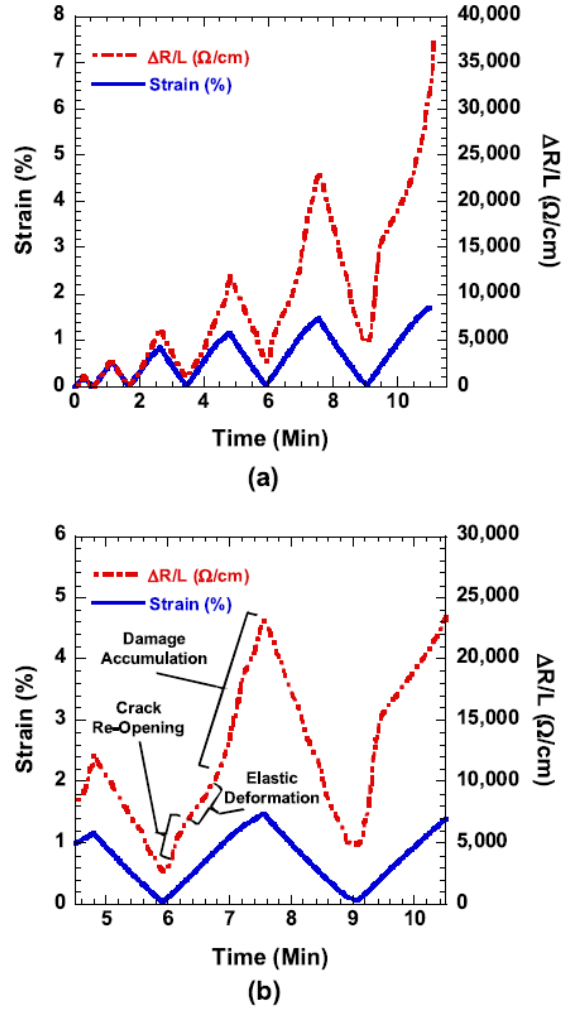Figure 25 shows the unloading curve for the fifth cycle and the loading curve for the sixth cycle. The fifth unloading cycle, indicated by the dashed line, shows crack closure as progressive steps in the resistance unloading curve. When the applied load is zero there is some permanent resistance change, ΔR_p. On the loading portion of the sixth cycle there is a clear increase in resistance at low strain followed by a linear region of elastic loading. In order to account for the portion of the resistance change on reloading due to crack re-opening, ΔR_{CO}, the amount of resistance that is related to elastic strain can be subtracted by extrapolating back to initial strain using a linear fit on the elastic portion of the reloading curve, as illustrated in Fig. 25. The value of the linear fit at zero strain is then defined as the damaged resistance change, ΔR_D, which is composed of the crack re-opening resistance change, ΔR_{CO}, and the permanent resistance change, ΔR_p.
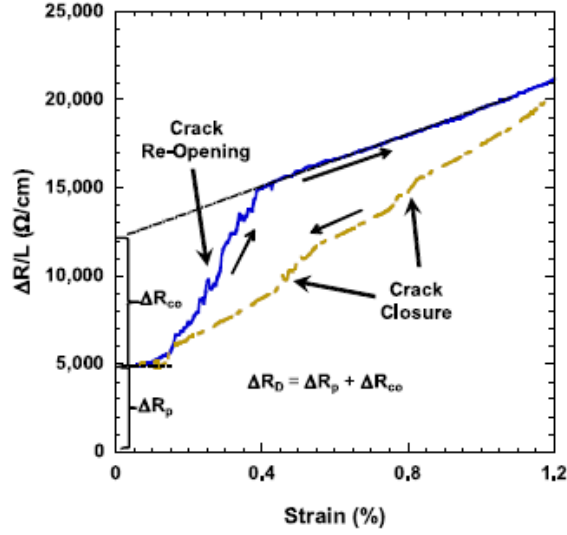
Fig. 25. Resistance change defined as a measure of damage [17]

A similar analysis of damage formation in cross-ply $[0/90_2/0]$ composites using percolating carbon nanotube networks was performed [18]. The unique damage progression is shown through the resistance behavior of a specimen in Fig. 26. The accumulation of cracks in the specimen is show in both optical micrographs and a schematic in Fig. 27.
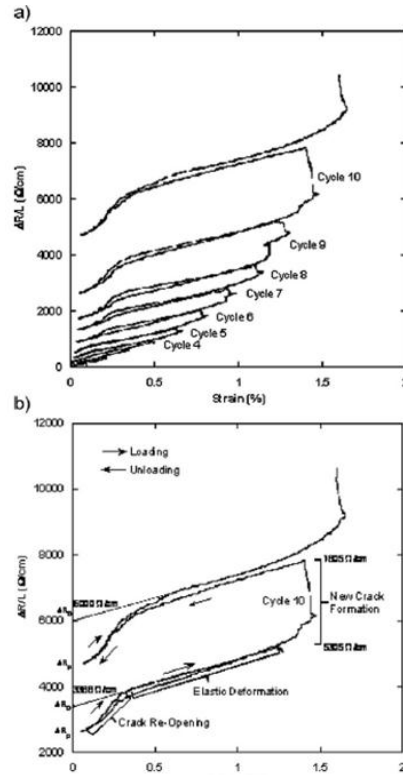
Fig. 26. a) Resistance/strain behavior showing hysteresis during cyclic loading and b) Analysis of a single cycle showing crack formation and re-opening behaviors and identification of the damaged resistance parameter, $\Delta R_D/L$ [18]
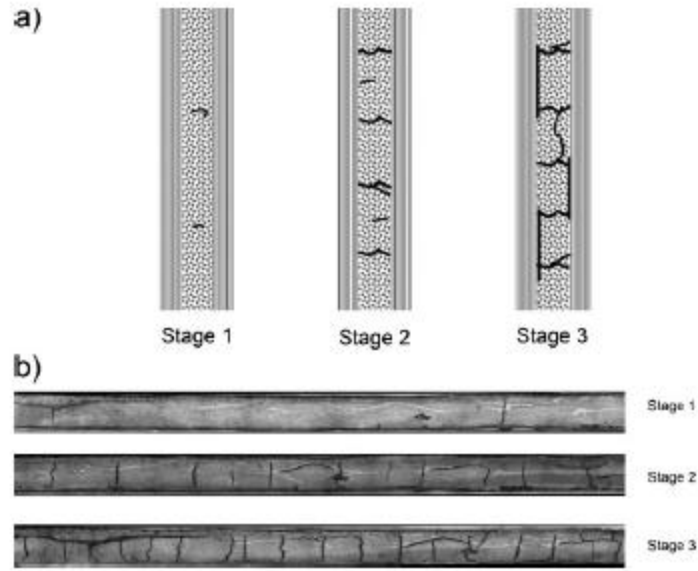
Fig. 27. a) Illustration of crack accumulation stages: microcrack initiation (Stage 1), transverse cracking (Stage 2) and ply delamination (Stage 3). b) Micrographs of edge replicas showing the accumulation of cracks at different stages [18]
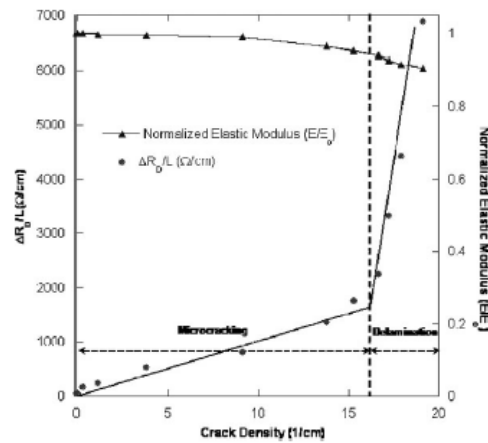
Fig. 28. Resistance and modulus changes for a [0/90/0] laminate as a function of crack density [18].

Figure 28 shows the damaged resistance change per length and the elastic modulus normalized with respect to the elastic modulus in the undamaged state, E0, as a function of crack density measured from edge replication.

The acoustic emissions marking the occurrence of damage in nanotube-based composites during tensile monotonic and cyclic loading are recorded, along with resistance [19]. The acoustic counts during a monotonic tensile test are plotted along with the mechanical and electrical response of a cross-ply composite specimens in Fig. 29.
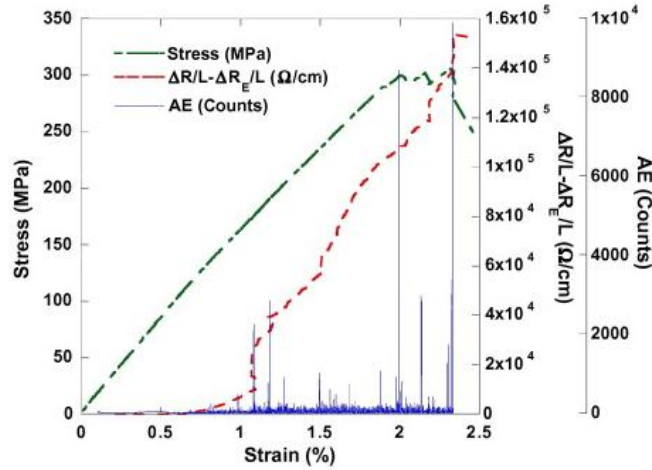
Fig. 29. Stress, AE (counts) and resistance change response to strain showing damage initiation, accumulation and delamination until failure during a quasi-static test [19].

The relation between resistance response and AE cumulative counts can be seen in Fig. 30. At the beginning of the test, the flaws and microcracks begin to disrupt the electrical network resulting in an increase in resistance. However, released energy from these flaws and microcracks are small and less detectable. As the applied load increases, the transverse cracks are formed progressively. These transverse cracks which are related to higher energy released AE signals break the path of electrical current. The following linear relationship of resistance change and AE counts indicates that damaged resistance can identify the material damage state quantitatively [19].
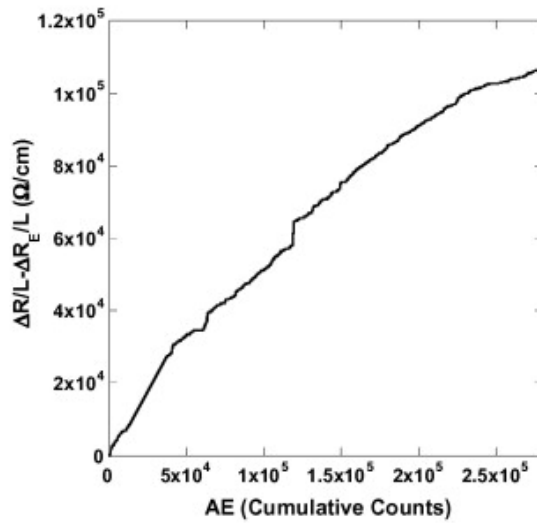
Fig. 30. The relationship between resistance change and AE (cumulative counts) [19]

F. Carbon Nanotube Science Reviews

Review articles covering the processing of carbon nanotube-based fibers and composites [20] and nanotube-based sensors and actuators [21] have been published under this grant. Specific topics discussed include the surface modification of single-walled carbon nanotubes, processing

methods (including wet-spinning, spinning from nanotube carpets and aerogels of nanotubes and twisting of single-walled carbon nanotube film), gel-spinning and electrospinning of carbon nanotube/polymer fibers, surface modification of advanced fibers using carbon nanotubes and nanotube orientation [20]. Particular emphasis is placed on damage sensing in nanotube-based composites and textile assemblies of carbon nanotubes. In discussing nanotube-based sensors and actuators, the charge distribution on carbon nanotubes, their electromechanical actuation, charge-induced failure and electrical conductivity and factors affecting these are presented [21].

Summary

Initial research into the development of carbon nanotube-based composites capable of self-sensing was focused on achieving electrical percolation in polymers using small amounts of carbon nanotubes. A calendering method was implemented to disperse nanotubes in epoxy and vinyl ester resins and it was demonstrated that electrical percolation occurred at nanotube concentrations of 0.1 wt%. An alternative processing method in which a carbon nanotube sizing agent was used to distribute nanotubes along the surface of glass fibers was also employed in the development of conductive composites.

Percolation models which identify the effect of nanotube concentration, waviness and tunneling distance on the electrical percolation threshold of nanotube-based composites were developed in order to improve the state-of-the-art processing methods. These nanotube networks within unreinforced and fiber reinforced composites were then demonstrated to be capable of sensing damage within the composite. Review articles summarizing the current progress into carbon nanotube development and capability for sensing and actuation have been written through the support of this grant.

References:

1. E. T. Thostenson and T. W. Chou, "Carbon Nanotube Networks: Sensing of Distributed Strain and Damage for Life Prediction and Self-Healing," *Advanced Materials*. **18**, 2837, 2006.
2. E. T. Thostenson and T. W. Chou, "Processing-structure-multi-functional property relationship in carbon nanotube/epoxy composites," Carbon. **44**(14):3022-3029, 2006.
3. L.M. Gao, T-W. Chou, E.T. Thostenson, A. Godara, Z.G. Zhang and L. Mezzo, "Highly conductive polymer composites based on controlled agglomeration of carbon nanotubes," *Carbon*. **48**(9):2649-2651, 2010.
4. H. S. Cokturk, T. J. Fiske, and D. M. Kalyon, " Effects of particle-shape and size distributions on the eelectrical and magnetic-properties of nickel/polyethylene composites," *J. Appl. Polym. Sci.* **50:**1891-1901, 1993.
5. E. J. Garboczi, K. A. Snyder, J. F. Douglas, and M. F. Thorpe, "Geometrical percolation-threshold of overlapping ellipsoids," *Phys. Rev. E* **52:**819, 1995.
6. N. Wagner, I. Balberg, and D. Klein, " Monte Carlo results for continuum percolation in low and high dimensions," *Phys. Rev. E* **74:**011127, 2006.
7. T. Ota, M. Fukushima, Y. Ishigure, H. Unuma, M. Takahashi, Y. Hikichi, and H. Suzuki, " Control of percolation curve by filler particle shape in Cu-SBR composites," *J. Mater. Sci. Lett.* **16:**1182, 1997.

8. M. L. Clingerman, E. H. Weber, J. A. King, and K. H. Schulz, " Development of an additive equation for predicting the electrical conductivity of carbon-filled composites," *J. Appl. Polym. Sci.* **88:**2280, 2003.
9. C. Y. Li and T. W. Chou, "Continuum percolation of nanocomposites with fillers of arbitrary shapes," *Applied Physics Letters,* **90,** 174108, 2007.
10. C. Li, E.T. Thostenson and T-W. Chou "Effect of Nanotube Waviness on the Electrical Conductivity of Carbon Nanotube-Based Composites," *Composites Science and Technology.* **68**(6):1227-1249, 2008.
11. C. Li, E.T. Thostenson and T-W. Chou "Dominant Role of Contact Resistance in Electrical Conductivity of Carbon Nanotube-Based Composites," *Applied Physics Letters.* **91**:223114 2007.
12. T. W. Ebbesen, H. J. Lezec, H. Hiura, J. W. Bennett, H. F. Ghaemi, and T. Thio, " Electrical conductivity of individual carbon nanotubes," *Nature (London).* **382:**54, 1996.
13. M. S. Fuhrer, J. Nygard, L. Shih, M. Forero, Y. G. Yoon, M. S. C. Mazzoni, H. J. Choi, J. Ihm, S. G. Louie, A. Zettl, and P. L. McEuen, "Crossed nanotube junctions," *Science* **288**:494, 2000.
14. C. Li and T-W. Chou "Direct Electrifying Algorithm for Backbone Identification," *Journal of Applied Physics A: Mathmatical and Theoretical,*" **40:**14679–14686, 2007.
15. C. Y. Li and T. W. Chou, "Theoretical studies on the charge-induced failure of single-walled carbon nanotubes," *Carbon*, **45**, 922-930, 2007.
16. C.Y. Li and T.W. Chou, "Electrostatic charge distribution on single-walled carbon nanotubes," *Appl Phys Lett* **89**:063103, 2006.
17. E.T. Thostenson and T-W. Chou "Real-Time *in situ* Sensing of Damage Evolution in Advanced Fiber Composites using Carbon Nanotube Networks," *Nanotechnology*, **19**(21):215713, 2008.
18. L.M. Gao, E. T. Thostenson, Z.G. Zhang, T-W. Chou, "Sensing of damage mechanisms in fiber-reinforced composites under cyclic loading using carbon nanotubes," *Advanced Functional Materials* **19**:123-130, 2009.
19. L.M. Gao, E.T. Thostenson, Z.G. Zhang, J-H. Byun, T-W. Chou, "Coupled carbon nanotube network and acoustic emission monitoring for sensing of damage development in composites," *Carbon* **47**(5):1381-1388, 2009.
20. T-W. Chou, L.M. Gao, E.T. Thostenson, Z.G. Zhang and J-H. Byun, "An assessment of the science and technology of carbon nanotube-based fibers and composites" *Composites Science and Technology.* **70**(1):1-19, 2010.
21. C. Li, E.T. Thostenson and T-W. Chou "Sensors and Actuators Based on Carbon Nanotubes and Their Composites: A Review," *Composites Science and Technology*, **68**(6):1227-1249, 2008.

Personnel Supported:

Tsu-Wei Chou, Principal Investigator
Erik T. Thostenson, Co-Principal Investigator
Chunyu Li, Ph.D.
Limin Gao, Graduate Student

Group Publications (GP) During Current Grant Period:

1. E. T. Thostenson and T. W. Chou, "Carbon Nanotube Networks: Sensing of Distributed Strain and Damage for Life Prediction and Self-Healing," *Advanced Materials,* **18**, 2837, 2006.
2. C. Y. Li and T. W. Chou, "Continuum percolation of nanocomposites with fillers of arbitrary shapes," *Applied Physics Letters,* **90,** 174108, 2007.
3. C. Y. Li and T. W. Chou, "Theoretical studies on the failure of charged single-walled carbon nanotubes," *Carbon*, **45**, 922-930, 2007.
4. C. Li and T-W. Chou "Direct Electrifying Algorithm for Backbone Identification," *Journal of Applied Physics A: Mathmatical and Theoretical*, **40**, 14679–14686, 2007.
5. C. Li, E.T. Thostenson and T-W. Chou "Dominant Role of Contact Resistance in Electrical Conductivity of Carbon Nanotube-Based Composites," *Applied Physics Letters*, **91**, 223114, 2007.
6. C. Li, E.T. Thostenson and T-W. Chou "Effect of Nanotube Waviness on the Electrical Conductivity of Carbon Nanotube-Based Composites," *Composites Science and Technology*, **68**(6) 1227-1249, 2008.
7. C. Li, E.T. Thostenson and T-W. Chou "Sensors and Actuators Based on Carbon Nantubes and Their Composites: A Review," *Composites Science and Technology*, **68**(6) 1227-1249, 2008.
8. E.T. Thostenson and T-W. Chou "Real-Time *in situ* Sensing of Damage Evolution in Advanced Fiber Composites using Carbon Nanotube Networks," *Nanotechnology*, **19**(21) 215713, 2008.
9. L.M. Gao, E. T. Thostenson, Z.G. Zhang, T-W. Chou, "Sensing of damage mechanisms in fiber-reinforced composites under cyclic loading using carbon nanotubes," *Advanced Functional Materials* **19**:123-130, 2009.
10. L. M. Gao, E. T. Thostenson Z. G. Zhang and T-W. Chou, "Coupled Carbon Nanotube Network and Acoustic Emission Monitoring for Sensing of Damage Development in Composites," *Carbon*, **47**(5): 1381-1388, 2009.
11. C. Y. Li and T-W. Chou, "Electrical Conductivities of Composites with Aligned Carbon Nanotubes," *Journal of Nanoscience and Nanotechnology*, **9**(4): 2518-2524, 2009.
12. C. Y. Li and T-W. Chou, "Precise Determination of Backbone Structure and Conductivity of 3D Percolation Networks by the Direct Electrifying Algorithm," *International Journal of Modern Physics C*, **20**(3): 423-433, 2009.
13. C. Y. Li and T-W. Chou, "Modeling of damage sensing in fiber composites using carbon nanotube networks," *Composites Science and Technology*, **68**(15-16): 3373-3379, 2008.
14. Tsu-Wei Chou, Limin Gao, Erik T. Thostenson, Zuoguang Zhang and Joon-Hyung Byun, "An assessment of the science and technology of carbon nanotube-based fibers and composites" *Composites Science and Technology* **70**(1):1-19, 2010.
15. Limin Gao, Tsu-Wei Chou, Erik T. Thostenson, Ajay Godara, Zuoguang Zhang and Luca Mezzo, "Highly conductive polymer composites based on controlled agglomeration of carbon nanotubes" *Carbon* **48**(9):2649-2651, 2010.

Interactions/Transitions:
(a) Participation/presentations at meetings, conferences, seminars, etc. during report period:

1. C. Li and T. W. Chou, "Charge Distributions on Single-Walled Carbon Nantubes by an Atomistic Moment Method," *Proceedings of the American Society for Composites – Twentieth Technical Conference*, Philadelphia, Sep. 9-14, 2006.
2. E. T. Thostenson and T. W. Chou, "Multifunctional Carbon Nanotube/Epoxy Composites: Processing and Characterization," *Proceedings of the 38th International SAMPE Technical Conference*, Dallas, TX, November 6-9, 2006.
3. E. T. Thostenson and T. W. Chou, "Multifunctional Carbon Nanotube/Epoxy Composites: Processing and Characterization," *Proceedings of the 38th International SAMPE Technical Conference*, Dallas, TX, November 6-9, 2006.
4. E. T. Thostenson and T. W. Chou, "Multi-Scale Hybrid Nanotube/Fiber Composites: Processing and Characterization," *Proceedings of the 8th International Conference on Textile Composites (TEXCOMP-8),* Nottingham UK, October 16-18, 2006.
5. E. T. Thostenson, V. Gendlin and T-W. Chou, "Carbon Nanotube Composites for Self-Sensing of Deformation and Damage," Proceedings of the *52nd International SAMPE Symposium and Exhibition,* June 3-7, 2007, Baltimore, Maryland.
6. E. T. Thostenson and T. W. Chou, "Multifunctional Composites with Self-Sensing Capabilities: Carbon Nanotube-Based Networks," *SPIE Smart Structures and Materials & Nondestructive Evaluation and Health Monitoring (SS/NDE) 2007*, Proceedings of SPIE Volume: 6526, San Diego, CA, March 18-22, 2007.
7. E. T. Thostenson and T. W. Chou, "Influence of Reinforcement Morphology on Nanocomposite Fracture Behavior," *Proceedings of 16th European Conference on*
8. E. T. Thostenson and T. W. Chou, "Scalable Processing Techniques for Nanotube-Based Polymer Composites*," Proceedings of the 16th International Conference on Composite Materials*, Kyoto, Japan, 2007.
9. E. T. Thostenson and C. Li, "Carbon Nanotube-Based Composites for Damage Detection and Health Monitoring," *Proceedings of the 16th International Conference on Composite Materials*, Kyoto, Japan (Keynote), 2007.
10. E. T. Thostenson, L. M. Gao, T. W. Chou, "Carbon nanotube networks: in situ sensing of damage evolution in fiber composites," *Proceedings of the 40th International SAMPE Technical Conference*, Memphis, TN, September 8-11, 2008.
11. E. T. Thostenson, L. M. Gao, T. W. Chou, "Advances in the Science and Technology of Carbon Nanotube Composites," *Proceedings of the 17th International Conference on Composite Materials (ICCM-17)*, Edinburgh, Scotland, July 27-31, 2009.

(b) Consultative and advisory functions during report period:

During the reporting period, Tsu-Wei Chou has served as an advisor/reviewer on several committees, including:
- The Australian Research Council
- AIAA Fellow Selection Review Committee
- NSF NIRT Program Review Panel
- Air Force Minority Leaders Nanocomposite Program
- NSERC (Ottowa, Canada)
- Agency of Science
- Technology and Research (A*STAR), Singapore
- Qatar National Research Fund (QNRF)

- Japan Society for the Promotion of Science
- Stanford University-Composites Design Workshop

Honors/Awards:

Tsu-Wei Chou
2006   Fellow, American Institute of Aeronautics & Astronautics
2008   Fellow, The Minerals, Metals & Materials Society
2009   Medal of Excellence in Composite Materials, University of Delaware Center for
          Composite Materials

Erik T. Thostenson
2007   Elsevier Young Composites Researcher Award, American Society for Composites
2009   Young Investigator Program (YIP) Award, Air Force Office of Scientific Research

Prior to Current Grant Period:

Tsu-Wei Chou
1964-5 Walter P. Murphy Fellowship, Northwestern University
1966-7 Ford Foundation Fellowship, Stanford University
1970-1 Frederick Gardner Cottrell Fellowship, Research Corporation
1976   Senior Visiting Research Fellowship, British Science Research Council
1986-7 Fellow, Institute for Advanced Study, University of Delaware
1988   Special Faculty Award, College of Engineering, University of Delaware
1989-   Named Professor, University of Delaware
1994   Honorary Research Professor, Beijing University of Aeronautics & Astronautics, China
1996   Charles Russ Richards Memorial Award, American Society of Mechanical Engineers
1997   Honorary Research Professor, Northwestern Polytechnical University, China
1998   Distinguished Research Award, American Society for Composites
1998   Fellow, American Society of Mechanical Engineers
1999   Fellow, ASM International
2001   Fellow, American Society for Composites
2001   Francis Alison Medal, University of Delaware
2002   Associate Fellow, American Institute of Aeronautics & Astronautics
2002   Fellow, American Ceramic Society
2002   Highly Cited Researchers, ISI
2002   Worcester Reed Warner Medal, ASME
2003   Pierre S. du Pont Chair of Engineering

Erik T. Thostenson

1994   Society of Plastics Engineers Scholarship
1995-8 ARO/URI Fellowship
1997   C. E. Birchenall Award for Best Student Presentation, Brandywine Valley Chapter of
          ASM International
1998   Hoechst Celanese Excellence in Engineering Award

1999 Directors' Award, Center for Composite Materials
2000-1 University of Delaware Competitive Fellowship
2002 Outstanding Graduate Student Award - 1st Place Ph.D. Student Symposium, Society for the Advancement of Material and Process Engineering (SAMPE)
2004 Hayashi Memorial International Award, Japan Society for Composite Materials
2004 Alan P. Colburn Prize for Best Dissertation in the Mathematical and Engineering Sciences, University of Delaware
2004 R.L McCullough Scholar's Award, Center for Composite Materials